



PCT/AU00/00719

REC'D 18 JUL 2000

WIPO

PCT

Patent Office
Canberra

4

I, LEANNE MYNOTT, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PQ 1188 for a patent by WOODSIDE ENERGY LIMITED filed on 24 June 1999.

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

WITNESS my hand this
Seventh day of July 2000

LEANNE MYNOTT
TEAM LEADER EXAMINATION
SUPPORT AND SALES



ORIGINAL
AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

Invention Title: "Natural Gas Hydrate and Method for Producing Same"

The invention is described in the following statement:

NATURAL GAS HYDRATE AND METHOD FOR PRODUCING SAME

FIELD OF THE INVENTION

The present invention relates to a natural gas hydrate. More particularly, the present invention relates to a natural gas hydrate with improved gas content and stability characteristics and a method for producing the same.

BACKGROUND ART

Natural gas hydrates are a stable solid comprising water and natural gas, and have been known to scientists for some years as a curiosity. More recently, natural gas hydrates became a serious concern in regard to the transportation and storage of natural gas industries in cold climates, due to the tendency of hydrates to form in pipelines thereby blocking the flow the pipelines.

Natural gas hydrates may be formed by the combination of water and gas at relatively moderate temperatures and pressures, with the resulting solid having the outward characteristics of ice, being either white or grey in colour and cold to the touch. At ambient temperatures and pressures natural gas hydrates break down releasing natural gas.

The potential uses of natural gas hydrates are diverse, ranging from a means for enabling the convenient transport and storage of natural gas to providing a means for the disposal of green house gases.

Conventionally, gas storage is achieved through re-injecting into reservoirs, or pressurised reservoirs or through the use of line pack, where the volume of the pipeline system is of the same order of magnitude as several days customer consumption. The use of natural gas hydrates in storage has the potential to provide a flexible way of storing reserves of natural gas to meet short to medium term requirements in the event of excessive demands or a reduction in the delivery of gas from source.

In any application, the gas content of the hydrate and the temperature at which the hydrate begins to decompose, the hydrate desolution temperature, are significant criteria that require consideration. Known natural gas hydrates exhibit a maximum gas content of 163 Sm^3 per m^3 of hydrate, and a hydrate desolution
5 temperature, at atmospheric pressure, of -15°C .

It is one object of the present invention to provide a natural gas hydrate and a method for the production thereof, with improved maximum gas content and hydrate desolution temperature.

Throughout the specification, unless the context requires otherwise, the word
10 "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

DISCLOSURE OF THE INVENTION

In accordance with the present invention there is provided a natural gas hydrate
15 with a maximum gas content in excess of 163 Sm^3 per m^3 . Preferably, the natural gas hydrate has a maximum gas content in excess of 170 Sm^3 per m^3 . Preferably still, the natural gas hydrate has a maximum gas content in excess of 180 Sm^3 per m^3 . Further and still preferably, the natural gas hydrate has a maximum gas content of 186 Sm^3 per m^3 .

20 Preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -15°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -13°C at atmospheric pressure. Further and still preferably, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric
25 pressure.

In accordance with the present invention, there is further provided a natural gas hydrate which exhibits a hydrate desolution temperature in excess of -15°C at atmospheric pressure. Preferably, the natural gas hydrate exhibits a hydrate

desolution temperature in excess of -13°C at atmospheric pressure. Preferably still, the natural gas hydrate exhibits a hydrate desolution temperature in excess of -11°C at atmospheric pressure.

Preferably, the natural gas hydrate has a maximum gas content in excess of $163 \text{ Sm}^3 \text{ per m}^3$. Preferably still, the natural gas hydrate has a maximum gas content in excess of $170 \text{ Sm}^3 \text{ per m}^3$. Further and still preferably, the natural gas hydrate has a maximum gas content in excess of $180 \text{ Sm}^3 \text{ per m}^3$. In a highly preferred form of the invention, the natural gas hydrate has a maximum gas content of $186 \text{ Sm}^3 \text{ per m}^3$.

10 In accordance with the present invention there is still further provided a method for the production of the natural gas hydrate of the present invention, the method comprising the steps of:-

15 combining natural gas, water to form a natural-gas water system and an agent adapted to reduce the natural-gas-water interfacial tension to form a natural-gas water-agent system;

allowing the natural gas-water-agent system to reach equilibrium at elevated pressure and ambient temperature;

reducing the temperature of the natural gas-water-agent system to initiate the formation of the natural gas hydrate.

20 Preferably, the agent is a compound that is at least partially soluble in both water and natural gas. Preferably still, the agent is an alcohol. In a highly preferred form of the present invention, the agent is isopropyl alcohol.

The quantity of the agent added to the natural gas-water system depends on the nature of the agent. However, preferably the agent is added in a quantity below about 1.0% by volume of water. Preferably still, the agent is added in a quantity
25 below about 0.5% by volume of water. Where the agent is isopropyl alcohol, the agent is added in a quantity of about 0.1% by volume of water.

The degree to which the temperature is decreased depends upon the degree to which the pressure is elevated. However, preferably the pressure exceeds about 50 bars and preferably, the temperature is below about 18°C.

5 Preferably, the natural-gas-water-agent system is constantly mixed throughout the hydration process.

EXAMPLES

The present invention will now be described in relation to four examples. However, it must be appreciated that the following description of those examples is not to limit the generality of the above description of the invention.

10 Hydrate Formation

Example 1

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly
15 by bubbling the methane through the water phase. The system was stabilised at a pressure of 206 bars (3000psia) and room temperature of 23°C

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 17.7°C. Crystals of methane hydrate were observed on the sapphire window, and hydrate formation was assumed to be complete when
20 pressure had stabilised in the cell.

Example 2

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium pressure for a normal water-methane system. Equilibrium was achieved quickly

by bubbling the methane through the water phase. The system was stabilised at a pressure of 138 bars (2000psia) and room temperature of 23°C

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 15.5°C. Crystals of methane hydrate were observed on
5 the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

Example 3

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium
10 pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at a pressure of 102 bars and room temperature of 23°C

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 13.1°C. Crystals of methane hydrate were observed on
15 the sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

Example 4

Water and isopropyl alcohol (0.1% by volume) were introduced into a sapphire cell. The cell was pressurised with methane gas above the hydrate equilibrium
20 pressure for a normal water-methane system. Equilibrium was achieved quickly by bubbling the methane through the water phase. The system was stabilised at a pressure of 54.5 bars (800psia) and room temperature of 23°C

The temperature was then reduced at a rate of 0.1°C per minute using a thermostat air bath to 8.1°C. Crystals of methane hydrate were observed on the
25 sapphire window, and hydrate formation was assumed to be complete when pressure had stabilised in the cell.

Testing desolution temperature and natural gas content of hydrate

Having formed the hydrate as outlined in Example 1, excess methane was removed and the temperature of the system was reduced to -15°C , at a rate of 0.1°C per minute, and the pressure of the system was observed to diminish to
5 zero.

The hydrate was stored for more than 12 hours at -15°C , showing no observable changes in appearance. The pressure remained at zero throughout.

After 12 hours, the temperature of the system was gradually increased at a rate of 0.2°C per minute, in an attempt to reverse the hydrate formation process.
10 Throughout this stage the pressure of the system was carefully monitored and recorded by way of high precision digital pressure gauges. The pressure of the system remained stable until the temperature reached -11.5°C , at which point some increase was noted. The pressure continued to increase as the temperature increased until the pressure of the system stabilised at 206.3 bars at
15 the ambient temperature of 23°C .

Quantities of methane and water generated from the desolution of the hydrate were measured, and the methane content of the methane hydrate was calculated to be 186 Sm^3 per m^3 .

Each unique mixture of hydrocarbon and water has its own hydrate formation
20 curve, describing the temperatures and pressures at which the hydrate will form, and it is envisaged that additional analysis will reveal optimum pressure and temperature combinations, having regard to minimising the energy requirements for compression and cooling.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Dated this twenty fourth day of June 1999.

Woodside Energy Limited
Applicant

Wray & Associates
Perth, Western Australia
Patent Attorneys for the Applicant(s)

